METHOD OF PRODUCING INTEGRAL, HARD NITRIDE LAYER ON TITANIUM/TITANIUM ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to products manufactured from titanium and/or titanium alloys having a hard, wear-resistant and pure nitride layer in the surface, and to a method of manufacturing such products.

Titanium and its alloys are used primarily in corrosive environments and in applications demanding a combination of good strength properties (ultimate stress limit, elasticity module, ductility) and low density. Titanium and titanium are generally used in this connection in the aviation industry. Thanks to the unique corrosion and biocompatibility properties of titanium, it is also used to make prostheses, e.g. parts for cardiac valves, load-carrying hip and knee joints, etc. Other areas requiring the unique corrosion resistance of titanium are in the biotechnical and chemical industries, where titanium and titanium alloys are used primarily for the material in valves and pump cylinders which are subjected to high pressure in combination with sliding contact and extremely high tightness requirements at the sliding surface. According to the present invention a nitride layer is formed on titanium or titanium alloys by means of surface conversion, this layer having extremely good friction, corrosion and biocompatibility properties, as well as extremely good adhesion to the substrate. Capillaries and the like are also provided with the nitride layer. The invention relates to products such as prosthesis shafts, wear-parts for prosthesis shafts, as well as valve parts and pump cylinders, manufactured out of titanium or titanium alloys, with a pure nitride layer of this type in the surface. The invention also relates to a method of manufacturing such products.

The purpose of the nitride layer is to improve wear, corrosion and friction properties in the surface of titanium or its alloys. This nitride layer improves the corrosion-proof and biocompatibility properties of the titanium or titanium alloy.

2. Description of Related Art

Several methods are already known to harden the surface of titanium and titanium objects. It is, for instance, known to oxide the surface of titanium by heating so that oxygen in the air combines with the titanium to give TiO_2 and forming an oxide layer. However, this oxide layer is neither very hard nor very thick and its properties are too poor for the applications mentioned above.

Another way of hardening the surface of titanium objects is to immerse them in a cyanide-based salt melt at a temperature of about 800° C. This treatment results in a mixed zone comprising nitrogen, carbon and a small proportion of oxygen. The thickness of the layer is about 0.035 mm at a hardness of 700 HV at the edge. This is the known Tiduran process according to Degussa. The method does not produce pure nitride since both oxygen and carbon are present. The corrosion and biocompatibility properties, as well as mechanical properties, hardness and adhesion to the substrate thus deteriorate.

The known ionic nitration is performed at treatment temperatures of 400° C. to 600° C. With the aid of abnormal corona discharge, nitrogen is created in ionized form and is included in the surfaces of the workpiece. The hardness values at the surface reach about 1500 HV. However, difficulties arise when treating the interior of workpieces, since the method is a so-called "line-of-fire process", and treating spherical surfaces or the like (e.g. joint prostheses).

Using the PVD (Physical Vapour Deposition) technique a surface layer of titanium nitride can be obtained. The PVD concept covers a large number of coating processes. However, two main principles can be distinguished: vaporization and sputtering. In the case of vaporization the coating material is heated in a vacuum chamber to a temperature at which vaporization occurs. Heating may be performed resistively, inductively or by irradiation with laser or electrons. The component to be coated is placed in the same chamber as the vaporization source. Since vaporization occurs under vacuum (10^{-2}–10^{-4} Pa), the vaporized atoms will move undisturbed in straight paths from the source to the surface of the component, where they are adsorbed and form small crystal cores which in time grow into a coating. In the case of sputtering the coating material is in the form of a solid plate which is placed on a negative potential (ca. 1 kV) in a vacuum chamber. The component to be coated is placed on earth and, when a vacuum has been achieved (10^{-3} Pa), argon gas is leaked into the chamber to a pressure in the vicinity of 1 Pa. This produces a corona discharge in the gas, whereupon the argon atoms are ionized to positive argon ions and are accelerated towards the cathode (usually known as the target). When the argon ions encounter the target they will, by resilient impact, dislodge the target atoms from the cathode plate. This is termed sputtering. The target atoms thus sputtered from the surface will travel through the chamber until they land on a surface and a coating is produced. All PVD methods are line-of-fire processes and internal coating of capillaries, for instance, is thus impossible and even coating bodies of spherical or similar shape is difficult. Furthermore, no chemical reaction occurs between the layer and the basic material and adhesion of the surface layer may therefore be poor. A layer is formed by deposition with this method.

Using the CVD (Chemical Vapour Deposition) method titanium nitride can be precipitated at increased temperature from a gas mixture, usually consisting of titanium tetrachloride, hydrogen and nitrogen (or some other nitrogen component, such as ammonia). In this process a chemical reaction is activated thermally, usually in a furnace. A gas mixture is conveyed to a reactor and a solid phase is deposited in the form of a surface coating on the heated object. Surface irregularities are covered very well in this method. However, in certain cases the method may give rise to poorer adhesion of the nitride layer due to the formation of chloride salts in the boundary layer between then titanium and the titanium nitride. With this method also, the layer is formed by deposition.

It is known that titanium and titanium alloys that are subjected to an atmosphere containing hydrogen at increased temperature very easily give hydrogen embrittlement, resulting in greatly deteriorated mechanical properties of both layer and substrate.

In the case of ion implantation a surface is irradiated with high-energy ions which penetrate into an alter the composition of the surface layer, and often also its structure. Modern equipment for ion implantation enables the implantation of sufficiently large doses within a